



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 785 578 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
23.07.1997 Bulletin 1997/30

(51) Int Cl. 6: H01L 27/092, H01L 51/20

(21) Application number: 97300063.1

(22) Date of filing: 07.01.1997

(84) Designated Contracting States:
DE FR GB

• Katz, Howard Edan
Summit, New Jersey 07901 (US)
• Dodabalapur, Ananth
Millington, New Jersey 07946 (US)

(30) Priority: 16.01.1996 US 587426

(74) Representative:
Watts, Christopher Malcolm Kelway, Dr. et al
Lucent Technologies (UK) Ltd,
5 Mornington Road
Woodford Green Essex, IG8 0TU (GB)

(71) Applicant: AT&T Corp.

New York, NY 10013-2412 (US)

(72) Inventors:

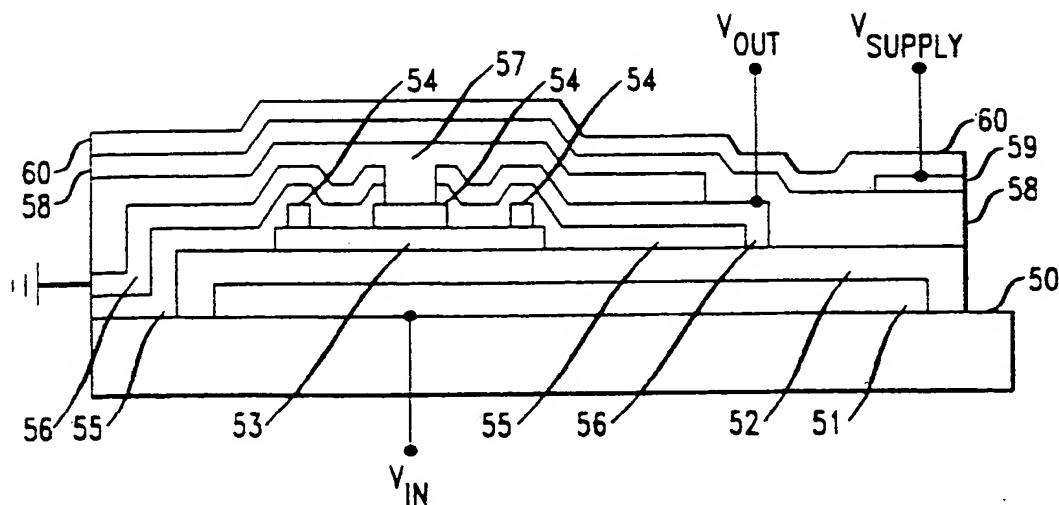
- Baumbach, Joerg
New Providence, New Jersey 07974 (US)

(54) Circuit comprising complementary thin film transistors

(57) Complementary circuits with inorganic n-channel thin film transistors (TFTs) (53,55) and organic p-channel TFTs (56,58,59) can exhibit advantageous properties, without being subject to some of the drawbacks of prior art complementary inorganic TFTs or complementary organic TFTs. In preferred embodiments of the invention, the n-channel inorganic TFTs

have an amorphous Si active layer (53), and the p-channel organic TFTs have α -hexathiophene (α -6T) active layer (58). Complementary inverters according to the invention are disclosed, as is an exemplary processing sequence that can be used to manufacture integrated complementary inverters and other complementary circuits according to the invention.

FIG. 9



BEST AVAILABLE COPY

Printed by Setice 75001 PARIS (F)

EP 0 785 578 A2

Description**Field of the Invention**

This invention pertains to articles that comprise complementary thin film transistors, in particular, to articles that comprise organic thin film transistors (organic TFTs).

Background of the Invention

Organic TFTs are known. See, for instance, US patent 5,347,144. However, until recently, attainable device parameters (e.g., on/off ratio) were insufficient for most contemplated applications (e.g., as pixel switches in active matrix liquid crystal displays). A. R. Brown (*Science*, Vol. 270, p. 972, November 1995) disclose logic gates made from polymer transistors.

Recently it has been demonstrated that organic TFTs (more specifically, organic TF field effect transistors or TF-FETs) can be produced to have on/off current ratios $> 10^6$ and switching speeds of about 10 μ s. See A. Dodabalapur et al., *Science*, Vol. 268, p. 270 (1995), and H. E. Katz et al., *Proceedings of the PMSE Division of the American Chemical Society*, Vol. 72, p. 467 (1995). See also EP-A-0716 458 and EP-A-0716459.

More recently still it was discovered that organic TF FETs can be designed such that a given device can function as a n-channel or p-channel device, depending on biasing conditions. See EP-A-0716459. See also A. Dodabalapur et al., *Science*, Vol. 269, p. 1560 (Sept. 1995).

As those skilled in the art will recognize, the organic TF FETs of EP-A-0716 459 can be combined to yield complementary circuits, with the attendant advantages of reduced power consumption and simplicity of circuit design.

The devices of EP-A-0716 459 comprise an organic p-channel material (exemplarily α -hexathiylene or α -6T) and an organic n-channel material (exemplarily C₆₀). Whereas α -6T can be a relatively stable material that is more easily deposited in p-type form than many inorganic semiconductors, C₆₀ and other organic materials that have been made to work as n-channel material typically undergo degradation when used in air. Thus such devices typically require unconventional manufacturing techniques and/or careful packaging in order to attain reasonable lifetimes. Such manufacturing and packaging would at best be expensive (and thus incompatible with many of the low cost applications envisaged for complementary organic TF FETs). The required hermetic packaging may even be incompatible with such contemplated applications as smart cards and RF identification tags, which frequently demand at least a modest degree of mechanical flexibility of the circuitry.

At least until the above referred-to technological difficulties with organic n-channel TF FETs are overcome, it would be of interest to have available a technology for

making complementary circuits that is capable of taking advantage of the excellent characteristics of known p-channel organic TF FETs and of n-channel inorganic TF FETs, e.g., amorphous Si TF FETs, without being subject to the problems currently typically associated with organic n-channel TF FETs and inorganic p-channel TF FETs. This application discloses such a technology.

Summary of the Invention

The invention is defined by the claims. In a broad aspect the invention is embodied in an article (e.g., a smart card, a RF identification tag, an active matrix liquid crystal display, a random access memory, a read-only memory) that comprises at least a first and a second transistor, the two transistors being operatively connected together. The first transistor is a n-channel transistor and the second transistor is a p-channel transistor. The article thus comprises a circuit with complementary transistors, typically a multiplicity of n-channel transistors and a multiplicity of p-channel transistors. The transistors typically are operatively interconnected by conventional means, and the article typically comprises means that facilitate provision of electrical power (including an electrical signal) to the transistors.

Significantly, the n-channel transistor is an inorganic thin film transistor, exemplarily comprising material selected from the group consisting of amorphous silicon (a-Si), polycrystalline silicon, CdSe, TiO₂, ZnO and Cu₂S and the p-channel transistor is an organic TFT.

The active layer of the p-channel organic TFT exemplarily comprises a member of the group consisting of

- 35 i) oligomers of thiophene with degree of oligomerization ≥ 4 and ≤ 8 , linked via their 2- and 5-carbons;
- ii) alternating co-oligomers of thienylene and vinylene with thiophenes as terminal groups and 3-6 thiophene rings, linked via their 2- and 5-carbons;
- iii) linear dimers and trimers of benzo[1, 2-b: 4, 5-b']dithiophene;
- iv) the above oligomers with substituents (e.g., alkyl substituents with 1-20 carbons) on the 4- or 5-carbons of the end thiophenes;
- v) tetracene, pentacene, and end-substituted derivatives thereof; and
- vi) composites of p, p'-diaminobiphenyls in polymer matrices.

50 Articles according to the invention thus comprise hybrid complementary TFTs, and thus combine advantageous features of the two involved technologies, namely, inorganic TFT and organic TFTs technologies. In currently preferred embodiment the active layer of the p-channel (organic) TFT is α -6T, and of the n-channel (inorganic) TFT is amorphous silicon (a-Si).

Brief Description of the Drawings

FIG. 1 schematically shows an exemplary complementary circuit, namely, an inverter; FIGS. 2 and 3 show the respective current-voltage characteristics of an exemplary n-channel a-Si TFT and an exemplary p-channel α -6T TFT; FIG. 4 shows the transfer characteristic of an exemplary inverter for a supply voltage of 7.2 V; and FIGS. 5-9 schematically illustrate significant steps in an exemplary process for making an integrated complementary circuit according to the invention.

Like reference numerals refer to like or analogous features in the figures.

Detailed Description of Exemplary Preferred Embodiments

We have discovered that a hybrid thin film technology that combines p-channel organic TFTs and n-channel inorganic TFTs can offer advantageous features (e.g., relatively good stability in air, reasonably high carrier mobility) while avoiding some of the shortcomings of the prior art technologies (e.g., relative instability of the organic n-channel material, low n-channel mobility). For the sake of definiteness, the discussion below will be in terms of preferred embodiments of the invention, namely, articles that comprise an a-Si (n-channel) TFT and an α -6T (p-channel) TFT.

The inventive approach was exemplarily demonstrated with a complementary inverter circuit (10) as shown in FIG. 1. The n-channel a-Si TFT (11) was fabricated on a glass substrate. The channel dimensions of the n-channel TFT exemplarily are about 8 and 9 μ m (width and length, respectively). Finished devices were packaged in a TO-8 header using conventional techniques. The p-channel α -6T TFT (12) was made on a thermally oxidized n-type Si wafer. The Si functions as the gate contact and the SiO_2 as the gate dielectric. Gold source and drain pads were photolithographically defined on top of the SiO_2 . The channel length and width of the exemplary p-channel TFT was 25 μ m and 250 μ m, respectively. α -6T was sublimed over the described structure at a pressure of 10^{-6} Torr to complete the organic TFT. Electrical contact to the source and drain were made through the thin (e.g., 50 nm) α -6T layer.

FIGS. 2 and 3 show the current-voltage characteristics of the n-channel and p-channel TFTs, respectively, with I_{DS} , V_{DS} and V_{GS} signifying, respectively, drain-source current, drain-source voltage, and gate-source voltage. The exemplary a-Si TFT has a field-effect mobility in the range 0.1-1 $\text{cm}^2/\text{V}\cdot\text{s}$, and the exemplary α -6T TFT has a field-effect mobility in the range 0.01-0.03 $\text{cm}^2/\text{V}\cdot\text{s}$. The threshold voltages of the exemplary a-Si and α -6T TFTs are -4 V and 200 meV, respectively. The channel dimensions of the n- and p-channel transistors were chosen so that the drain currents are approximate-

ly equal for similar absolute values of the drain-source voltage and gate voltage. However, channel dimensions of the devices can be scaled down to levels limited by the lithographic or patterning techniques employed. Using previously disclosed synthesis and purification techniques, α -6T TFTs with channel lengths as small as 1.5 μ m have been fabricated which possess current-voltage characteristics similar to that shown in FIG. 3.

Complementary inverters were made by interconnecting the above described devices as shown in FIG. 1, where the p-channel α -6T TFT functions as the load transistor. The resulting inverters were tested under a variety of bias conditions. The supply voltage was varied in the range 5-18 V, and the transfer characteristics measured. FIG. 4 shows exemplary transfer characteristics for a supply voltage of 7.2V.

For low values of input voltage V_{in} , the p-channel α -6T load transistor is on (since the gate-source voltage is negative), and the n-channel is off. The output voltage V_{out} substantially equals the supply voltage. As V_{in} is increased the n-channel a-Si transistor is gradually turned on. A further increase in V_{in} causes the p-channel device to be turned off and the n-channel device to be turned completely on. Similar behavior was achieved with the supply voltage as low as 5V. The inverter circuit was simulated using the software tool MICROCAP®. The device characteristics of the n- and p-channel transistors were input into the program and transfer characteristics simulated. The results of the simulation are shown in FIG. 4 along with the experimental data points. Excellent agreement is obtained between theory and experiment for $V_T = 3.7$ V, which is very close to the measured threshold voltage of the device. The simulation also indicates that lowering this threshold voltage will allow the inverter to operate with a lower supply voltage.

A significant feature of complementary circuits according to the invention is their manufacturability in integrated circuit form, i.e., with both n-channel and p-channel TFTs disposed on a common substrate. An exemplary manufacturing process will be described below. The process could be used, for instance, to produce integrated inverter circuits of the type shown in FIG. 1. Since the inverter is the simplest complementary circuit, availability of a process for manufacture of an integrated inverter circuit implies that more complex circuits can also be realized with a given technology.

Among the significant process steps are the following:

- 50 1) provision of an appropriate substrate (e.g., a glass or plastic body);
- 55 2) gate metal (e.g., Ta, Cr, Al) deposition and patterning. This gate is common to both n- and p-channel transistors;
- 55 3) gate dielectric (e.g., polyimide or other polymer

that can be deposited by spinning or spraying from a liquid base) deposition. The polymer typically is cured after deposition. For instance, we have successfully used a pre-imidized polyimide supplied by Nissan Chemical Company under the designation SE-1180. The dielectric was spun at 4000 RPM and cured at 120°C for 2 hours. The thickness of a single coating was about 70 nm. In some instances two coatings were used;

4) undoped a-Si deposition (typically by plasma-enhanced CVD or RF sputtering) and patterning. This material will form the active layer of the n-channel transistor. It is removed by etching from most areas except the n-channel regions;

5) deposition of an isolation layer (e.g., SiN, polyimide or other insulator). This layer serves to prevent electrical shorting between source and drain regions of the n-channel transistors; For example, a polyimide manufactured by Nissan Chemical Company (designated RN-812) can be used. It forms an about 1 μm thick film and has good insulation properties;

6) patterning of the isolation layer. Windows are defined at the regions which will become the source and drain of the n-channel device, and material is removed in the region away from the active n-channel device area;

7) deposition of n⁺ a-Si (e.g., by plasma CVD or sputtering). This material will serve to facilitate making electrical contact to the undoped a-Si active layer;

8) patterning of the n⁺ a-Si layer (by opening a window to the isolation layer in the gate region) so as not to short the source and drain regions.

9) deposition and patterning of source/drain contact metal (e.g., Al). The metal is patterned such that source and drain of the n-channel device are not shorted together. It is also patterned to connect the n-channel and p-channel transistors in the circuit. Consequently it extends to some extent towards the (as yet not defined) p-channel device, and will form the source contact of the p-channel device;

10) deposition of SiN, polyimide or other dielectric to isolate the source/drain metal from the organic active layer that will be deposited in the next step. Patterning to remove polyimide above the active region of the p-channel transistor;

11) deposition (e.g., by vacuum sublimation) of organic active material (e.g., α-6T);

5 12) deposition (e.g., by sputtering or vacuum evaporation) and patterning of the drain contact metal (e.g., Au, Ag) of the p-channel transistor. This metal layer is also connected to the positive supply voltage;

13) deposition of a final passivation layer (e.g., SiN, polyimide) to protect the circuit and the devices.

10 FIGS. 5-9 schematically illustrate the above fabrication process. In FIG. 5, numerals 50-53 designate, respectively, the substrate, common gate metal, gate dielectric, and patterned undoped a-Si. In FIG. 6, numerals 54 refer to the patterned isolation layer, and 55 refers to the patterned n⁺ a-Si layer. In FIG. 7, numerals 56 refer to the patterned source/drain metal layer. In FIG. 8, numeral 57 refers to the patterned isolation layer, 58 refers to the organic active layer (e.g., α-6T), 59 refers to the drain contact of the p-channel transistor, and 60 refers to the final passivation layer. Finally, FIG. 9 schematically shows the layer structure of an inverter according to the invention, with the various voltages (V supply, ground, V_{in} and V_{out}) indicated.

15 In an exemplary embodiment, the substrate (50) is 25 KAPTON®, gate metal layer (51) is 50 nm of Ta, gate dielectric layer (52) is about 70 nm of the above referred-to polyimide, and patterned active n-channel material (53) is 100 nm of undoped amorphous Si (deposited by plasma enhanced CVD, substrate at 250°C; patterned 30 by plasma etching). A 1 μm thick polyimide isolation layer is deposited (using the above referenced RN-812) and patterned (54) by etching in an oxygen plasma (300 m Torr, room temperature). A 50 nm layer of n⁺ a-Si (55) is deposited by plasma enhanced CVD and patterned. 35 Source/drain contact (56) (50 nm Al) is deposited and patterned. This metal also serves to connect the n-channel and p-channel transistors in the circuit, and for this reason extends somewhat towards the p-channel transistor and forms the source contact of the p-channel 40 transistor. A 1 μm layer (57) of the above referred-to polyimide is spun on and etched away from regions near the p-channel transistor. A 50 nm layer (58) of α-6T is deposited by sublimation without masking or patterning. The drain contact (59) of the p-channel transistor (50 45 nm Al) is deposited by sputtering and patterned. A final polyimide passivation layer (60) is spun on.

Claims

50 1. An article comprising a first and a second transistor, said first and second transistors being operatively connected together, the first transistor being a n-channel transistor and the second transistor being a p-channel transistor;

CHARACTERIZED IN THAT

55 the n-channel transistor (11) is an inorganic thin film transistor and the p-channel transistor (12)

is an organic thin film transistor.

2. Article according to claim 1, wherein the inorganic thin film transistor comprises an active layer comprising material selected from the group consisting of amorphous Si, polycrystalline Si, CdSe, TiO₂, ZnO and Cu₂S, and wherein the organic thin film transistor comprises an active layer comprising material selected from the group consisting of

5

- i) oligomers of thiophene with degree of oligomerization ≥ 4 and ≤ 8 , linked via their 2- and 5-carbons;
- ii) alternating co-oligomers of thienylene and vinylene, with thiophenes as terminal groups and 3-6 thiophene rings, linked via their 2- and 5-carbons;
- iii) linear dimers and trimers of benzo [1 2-b' 4,5-b'] dithiophene;
- iv) any of the oligomers of i) ii) and iii) with substituents on the 4- or 5-carbons of the end thiophenes;
- v) tetracene, pentacene, and end-substituted derivatives thereof; and
- vi) composites of p, p'-diaminobiphenyls in polymer matrices.

10

3. Article according to claim 2, wherein said substituents on the 4- or 5-carbons of the end thiophene are alkyl substituents with 1-20 carbons

30

4. Article according to claim 1, wherein the organic thin film transistor comprises an active layer that comprises α -hexathiophene.

35

5. Article according to claim 1 or claim 4, wherein the inorganic thin film transistor comprises an active layer that comprises amorphous silicon.

6. Article according to any of the preceding claims wherein said first and second transistors are operatively connected to form a complementary inverter circuit.

40

45

50

55

FIG. 1

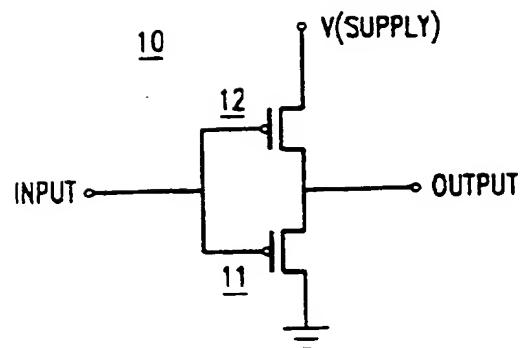


FIG. 2

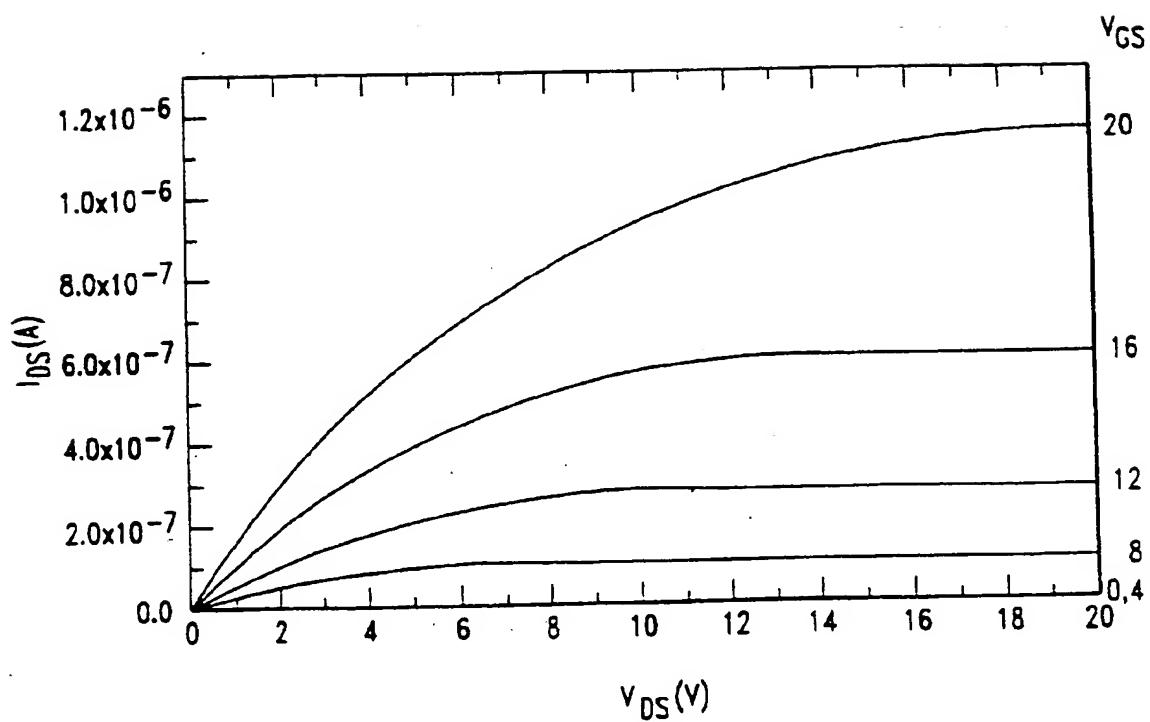


FIG. 3

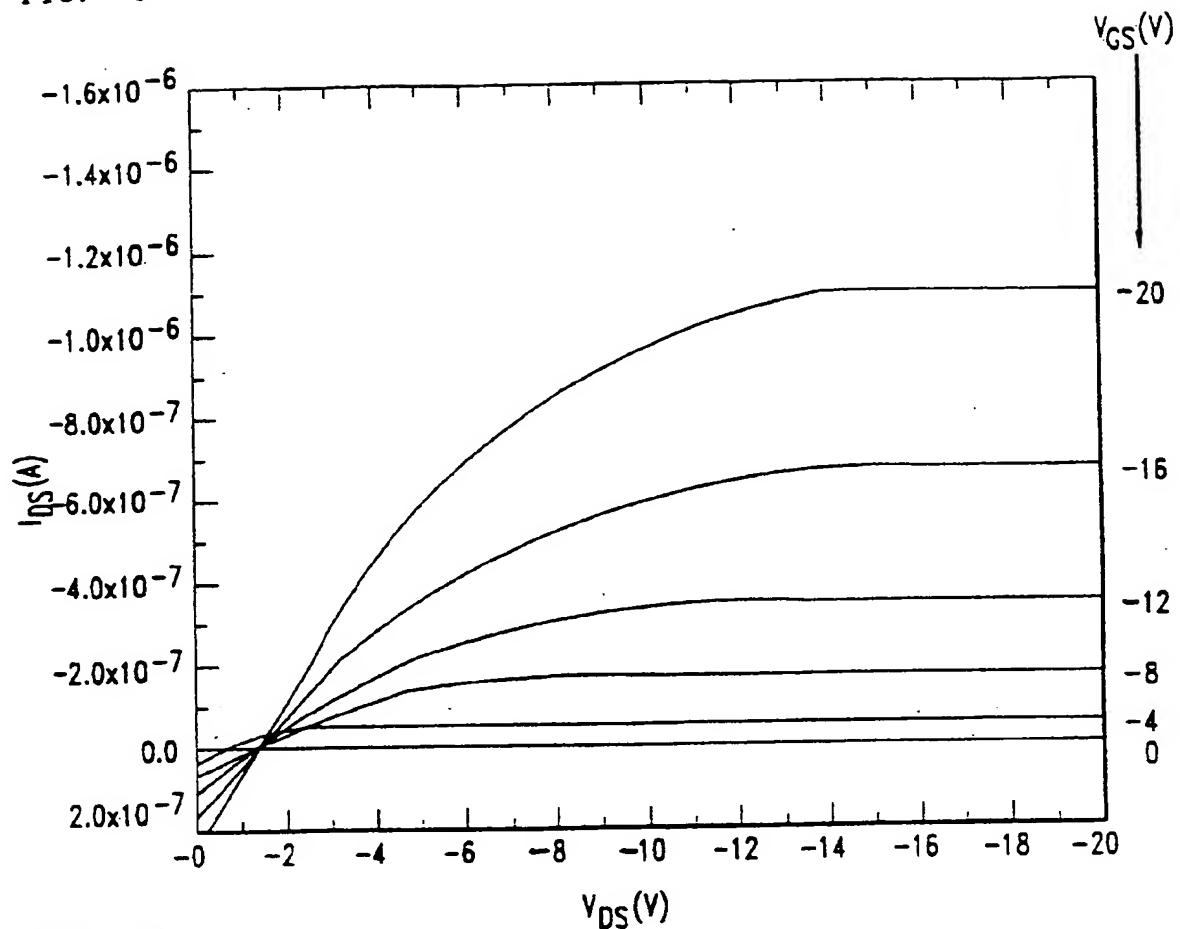


FIG. 4

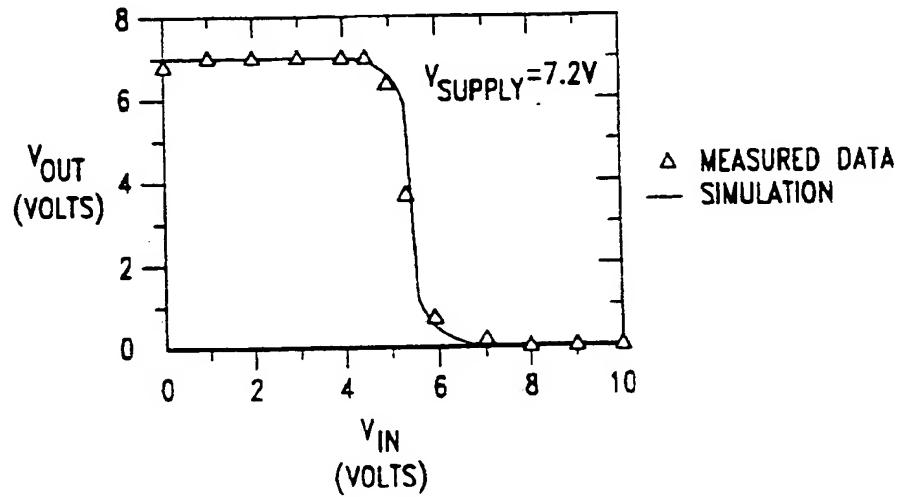


FIG. 5

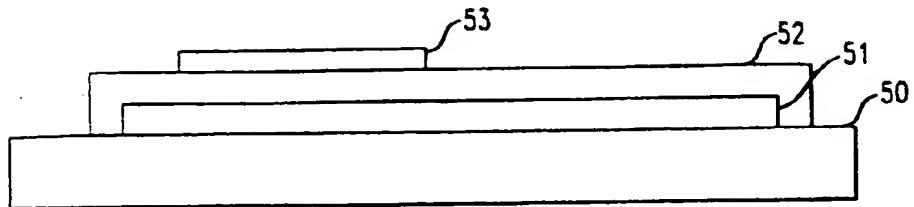


FIG. 6

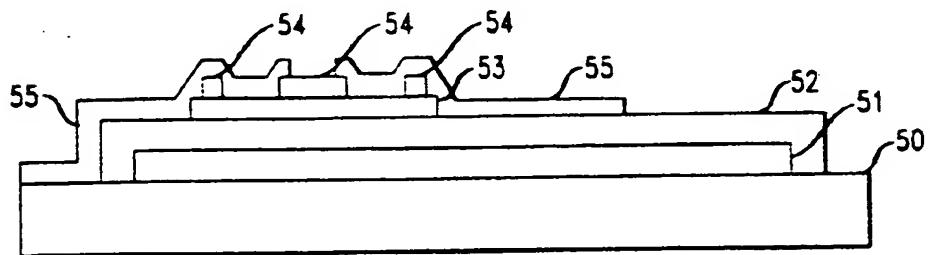


FIG. 7

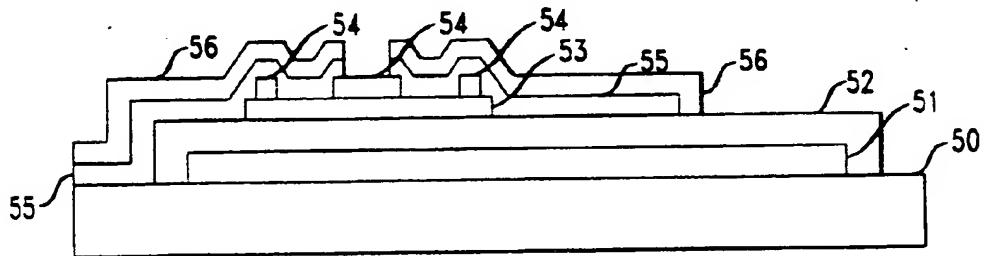


FIG. 8

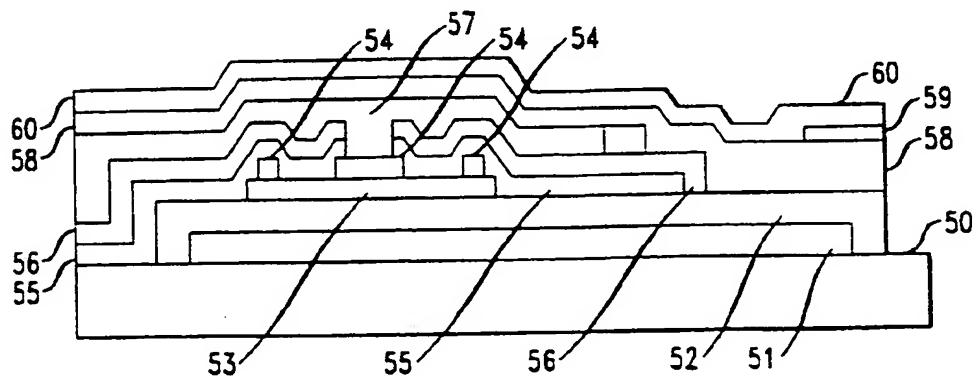
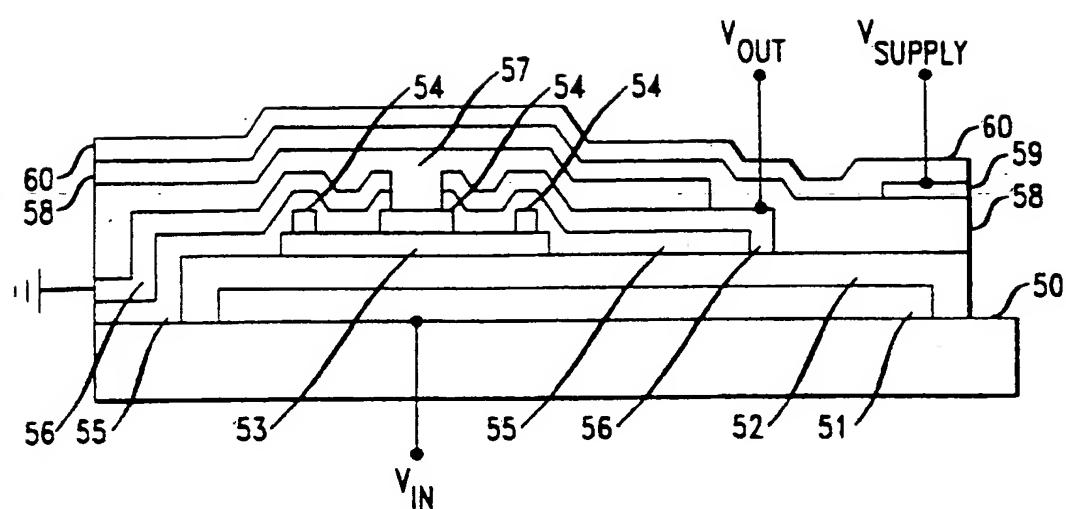


FIG. 9



(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11)



EP 0 785 578 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
22.04.1998 Bulletin 1998/17

(51) Int Cl. 6: H01L 51/20, H01L 51/30,
H01L 27/12

(43) Date of publication A2:
23.07.1997 Bulletin 1997/30

(21) Application number: 97300063.1

(22) Date of filing: 07.01.1997

(84) Designated Contracting States:
DE FR GB

• Katz, Howard Edan
Summit, New Jersey 07901 (US)

(30) Priority: 16.01.1996 US 587426

• Dodabalapur, Ananth
Millington, New Jersey 07946 (US)

(71) Applicant: AT&T Corp.
New York, NY 10013-2412 (US)

(74) Representative:
Watts, Christopher Malcolm Kelway, Dr. et al
Lucent Technologies (UK) Ltd,
5 Mornington Road
Woodford Green Essex, IG8 0TU (GB)

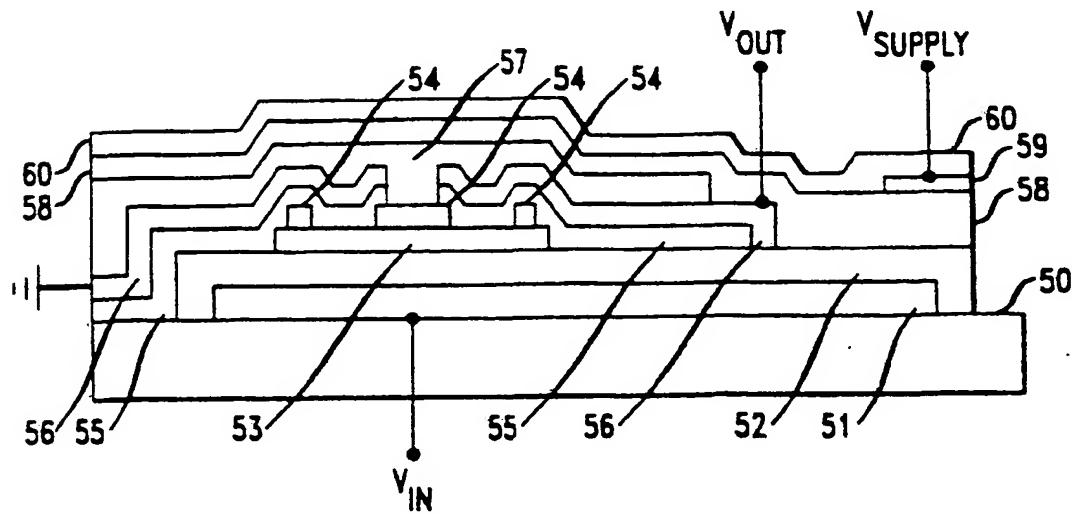
(72) Inventors:
• Baumbach, Joerg
New Providence, New Jersey 07974 (US)

(54) Circuit comprising complementary thin film transistors

(57) In preferred embodiments of the invention, the n-channel inorganic TFTs have an amorphous Si active layer (53), and the p-channel organic TFTs have α -hexathiienylene (α -6T) active layer (58). Complementary

inverters according to the invention are disclosed, as is an exemplary processing sequence that can be used to manufacture integrated complementary inverters and other complementary circuits according to the invention.

FIG. 9



EP 0 785 578 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 30 0063

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P, X	DODABALAPUR A ET AL: "Hybrid organic/inorganic complementary circuits" APPLIED PHYSICS LETTERS, 15 APRIL 1996. AIP, USA, vol. 68, no. 16, ISSN 0003-6951, pages 2246-2248, XP002055715 * the whole document *	1, 2, 4-6	H01L51/20 H01L51/30 H01L27/12
E	US 5 612 228 A (SHIEH CHAN-LONG ET AL) * column 2, line 3 - column 2, line 30: claims 1-18; figures 5,6 *	1, 2, 4-6	
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 016 (E-872), 12 January 1989 & JP 01 259563 A (MITSUBISHI ELECTRIC CORP), 17 October 1989, * abstract *	1, 2, 4	
D, A	DODABALAPUR A ET AL: "ORGANIC HETEROSTRUCTURE FIELD-EFFECT TRANSISTORS" SCIENCE, vol. 269, 15 September 1995, pages 1560-1562, XP000644688 -----		<p>TECHNICAL FIELDS SEARCHED (Int.Cl.6)</p> <p>H01L</p>
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner:	
THE HAGUE	16 February 1998	Königstein, C	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X	particularly relevant if taken alone		
Y	particularly relevant if combined with another document of the same category		
A	technological background		
C	non-written disclosure		
F	intermediate document		

EPO FORM 153A (1992-09-01)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.